

Calorimetric Study of 1-Butyl-1-Methylpyrrolidinium and Butyltrimethylammonium Bis(trifluoromethanesulfonyl)imide Ionic Liquids

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1-Alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ionic liquids (ILs) are the only ILs whose thermodynamic properties have been measured both in the condensed and gas phases. One of characteristic features of the bis(trifluoromethanesulfonyl)imide ILs is their ability to form multiple crystalline phases. In this work, we extend the range of the studied bis(trifluoromethanesulfonyl)imides to the ammonium and pyrrolidinium derivatives. The heat capacity of 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide [BuMePr]NTf₂ and butyltrimethylammonium bis(trifluoromethanesulfonyl)imide [BuMe₃N]NTf₂ over the temperature range of (5 to 370) K was measured in an adiabatic calorimeter with the uncertainty of $\pm 0.4\%$ at $T > 20$ K. [BuMePr]NTf₂ was found to form two different polymorphs. The parameters of fusion for the most stable polymorph were determined. The anomalous temperature dependence of heat capacity observed earlier for crystalline [C_nmim]NTf₂ at temperatures (10 to 50) K below their temperatures of fusion was also found in [BuMePr]NTf₂. It was demonstrated that the heat capacity of the crystals with that anomaly and without it was indistinguishable below the range of this anomaly. The thermal behavior of the ammonium salt was more complicated. Three sequences of crystalline phases each having a solid-phase transition were found for this compound. Thermodynamic parameters for all the phase transitions of [BuMe₃N]NTf₂ were determined. The increments for the 1,1-dialkylpyrrolidinium and tetraalkylammonium cations allowing one to calculate the entropies and heat capacities of corresponding ILs in the liquid state were derived.